

Effect of magnetism on the lattice dynamics in the σ -phase $Fe - Cr$ alloys

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Anomalies in the temperature dependences of the recoil-free factor, f , and the average center shift, $\langle CS \rangle$, measured by ^{57}Fe Mössbauer Spectroscopy, were observed for the first time in the archetype of the σ -phase alloys system, $Fe - Cr$. In both cases the anomaly started at the temperature close to the magnetic ordering temperature, and in both cases it was indicative of lattice vibrations hardening. As no magnetostrictive effects were found, the anomalies seem to be entirely due to a spin-phonon coupling. The observed changes in f and in $\langle CS \rangle$ were expressed in terms of the underlying changes in the potential, ΔE_p , and the kinetic energy, ΔE_k , respectively. The former, with the maximum value larger by a factor of six than the latter, decreases, while the latter increases with T . The total mechanical energy change, ΔE , was, in general, not constant, as expected for the Debye-like vibrations, but it resembled that of ΔE_p . Only in the range of 4-15 K, ΔE was hardly dependent on T .

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A thorough knowledge and good understanding of atomic lattice vibrations in solids, in general, and in technologically important materials, in particular, is essential, for the proper understanding of their physical properties such as thermal conductivity, heat capacity, vibrational entropy, Debye temperature, electron-phonon coupling as well as the noise of electronic devices. One of the open questions in the field is a possible relationship between magnetism and the lattice vibrations. The contribution of an electron-phonon interaction to magnetization of metallic systems is expected to be small, as, in general, $\frac{\hbar\omega_D}{E_F}$ is of the 10^{-2} order¹, where ω_D is the Debye cut-off frequency and E_F is the Fermi energy. Consequently, the effect of magnetism on the lattice dynamics in such systems should be rather negligible. However, following Kim¹ the effect of the electron-phonon coupling can be strongly enhanced below the Curie temperature, T_c , in an itinerant ferromagnet. A good candidate for verifying these predictions seem to be $\sigma - FeCr$ alloys which are believed to be itinerant ferromagnets with T_c -values below 50 K².

The σ -phase constitutes a broad class of binary and ternary alloy systems with common crystallographic structure ($D_{4h}^{14} - P4_2/mnm$) and physical properties depending on the system³. The $\sigma - FeCr$ which was discovered in 1923⁴ and identified in 1954⁵ has been known not only as the archetype of σ -phase, but mainly for scientific and technological reasons. The former stems from its interesting physical properties (e. g. complex crystallographic structure, high brittleness and hardness, low-temperature magnetism and unusually high value of the specific heat). The latter follows from the deteriorating effect of the phase presence on mechanical and corrosive properties of ferritic stainless steels that are regarded as important construction materials. Despite the phase has been known for over a half of a century, only few papers

relevant to its lattice vibrational properties have been published so far⁶⁻⁸. The Fe-partial phonon density of states (PDOS) of the $\sigma - FeCr$ was found to be significantly different from that of the $\alpha - FeCr$, which was not the case for the Debye temperatures of the two phases⁸. In this Letter an evidence obtained from Mössbauer spectroscopic (MS) study is reported that magnetism can significantly affect the lattice dynamics in σ -phase Fe-Cr samples.

MS is an exceptionally well-suited tool to study the atomic vibrations in solids as it delivers relevant information via two spectral parameters viz. the recoil-free factor, f , and the center shift, CS . The former is related to the mean-square amplitude of vibrations of the Mössbauer atoms, $\langle x^2 \rangle$, through the following equation,

$$f = \exp(-\langle x^2 \rangle k^2) \quad (1)$$

where k is the wave vector of the gamma radiation. The latter is a measure of the mean-square velocity of the vibrating atoms, $\langle v^2 \rangle$, via the second-order Doppler shift, SOD, given by,

$$SOD = -E_\gamma \langle v^2 \rangle / 2c^2 \quad (2)$$

where E_γ is the energy of the gamma rays.

In solids with no electron-phonon coupling, the temperature dependences of both CS and f are smooth monotonic decreasing functions of T . If, however, a strong enough spin-phonon coupling is present, an anomaly in the two quantities should be seen close to T_c .

Two samples of the σ -phase $FeCr$ alloys viz. $Fe_{54}Cr_{46}$ and $Fe_{52}Cr_{48}$ were the subject of the present study. They were obtained by an isothermal annealing of the bcc

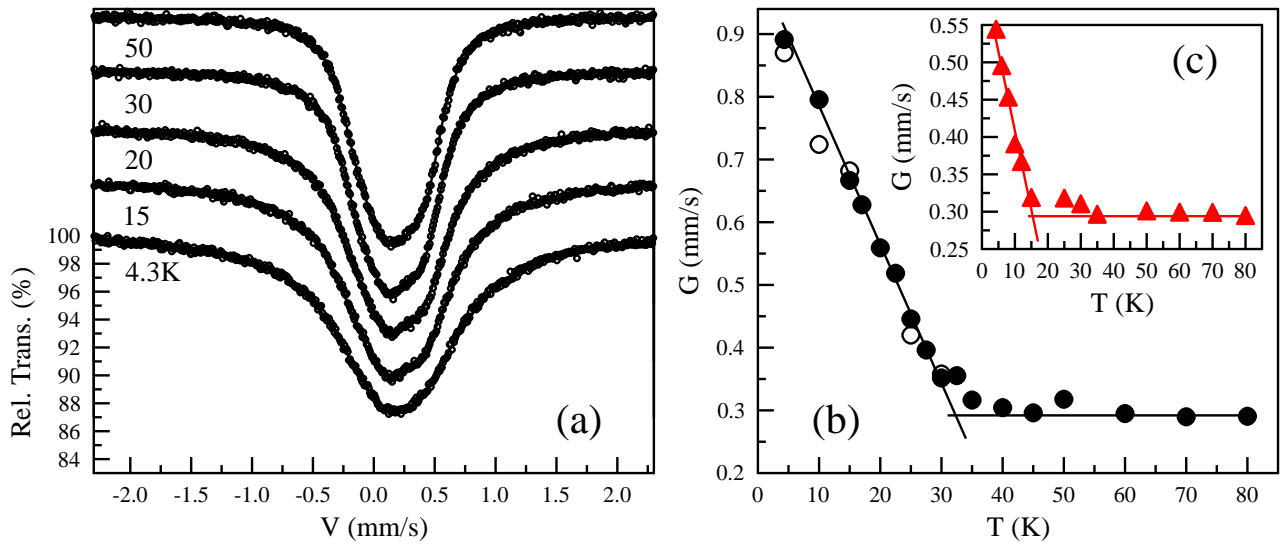


FIG. 1: (color online) (a) ^{57}Fe Mössbauer spectra recorded on $\sigma - \text{Fe}_{54}\text{Cr}_{46}$ at various temperatures shown in zero external magnetic field, and the full line width at half maximum, G , versus temperature for (b) $\sigma - \text{Fe}_{54}\text{Cr}_{46}$ and (c) $\sigma - \text{Fe}_{52}\text{Cr}_{48}$. The intersection of the lines defines the magnetic ordering temperature T_c . In (b) the data obtained for $\sigma - \text{Fe}_{54}\text{Cr}_{46}$ with a second run (open circles) are added.

master alloys at $T = 973$ K. More detailed description can be found elsewhere². In search for a possible effect of magnetism on the atomic vibrations, ^{57}Fe Mössbauer spectra were recorded in a transmission geometry at various temperatures, T , using a standard spectrometer, $^{57}\text{Co}/\text{Rh}$ source for the γ 14.4 keV radiation and a flowing cryostat that enabled stabilization of T with an accuracy of ± 0.1 K. Examples of the spectra recorded in this way can be seen in Fig. 1a. They were analyzed using a least-square iteration procedure. Among the fitted parameters were those pertinent to the present considerations viz. the width of the Lorentzian-shaped line, G , as well as the center shift, CS . A more detailed description of the procedure is given elsewhere⁶. From the temperature dependence of G , which can be seen in Figs. 1b,c, the value of the magnetic ordering temperature (Curie point), T_c , was determined. For $\text{Fe}_{54}\text{Cr}_{46}$ $T_c = 32.9$ K and for $\text{Fe}_{52}\text{Cr}_{48}$ $T_c = 15.2$ K were found. These values agree rather well with the corresponding figures of 38.9 K and 17.2 K, respectively, found from the magnetization data⁹.

The temperature dependence of the average center shift, $\langle CS \rangle$, as found from the fitting procedure, is illustrated in Fig. 2a. A smooth change of CS with T , as expected from the Debye model, can be seen until T reaches a certain critical value below which a steep decrease is observed. Data obtained with a second run of measurements for $\text{Fe}_{54}\text{Cr}_{46}$ are added, and they agree well with those obtained within the first run. The critical temperature at which the anomaly starts, 31.3 K and 16.3 K, for $\text{Fe}_{54}\text{Cr}_{46}$ and $\text{Fe}_{52}\text{Cr}_{48}$, respectively, was determined for each sample from the intersection of the curved lines, representing the behavior expected from

the Debye model, with the straight lines, representing the anomalous part of the data. A good agreement between the temperatures at which the anomalies in $\langle CS \rangle$ occur and the corresponding Curie temperatures, can be taken as evidence that the anomaly in $\langle CS \rangle$, hence in the atomic vibrations, is related to the magnetic state of the samples.

A further support to this supposition can be lend from the spectra measured at 4.2 K in an external magnetic field, B_o - see Fig. 3a. These spectra were analyzed in terms of a standard hyperfine field distribution method, assuming a linear correlation between the hyperfine field and the isomer shift. The values of $\langle CS \rangle$ derived from this approach are displayed in Fig. 3b versus the external magnetic field, B_o , showing a significant dependence on B_o . The increase of the amplitude of $\langle CS \rangle$ with B_o is equivalent to the increase of the mean-square velocity. The effect is consistent with the results found from the zero-field spectra - Fig. 2a.

Concerning now the f -factor, in the thin-absorber approximation, which was the case here, it is proportional to the spectral area, A . The $\ln(f')$, where $f' = A/A_o$, A_o being the spectral area at 80 K, is shown for both samples in Fig. 2b versus T . The right-hand axis is scaled in the underlying change of the mean-square amplitude of vibrations, $\Delta\langle x^2 \rangle$, relative to its value at 80 K. One can easily notice that an increase in $\ln(f')$ is observed for both samples below T close to the corresponding Curie points (indicated by arrows). The increase in f' on decreasing T is equivalent to the decrease of the mean-square amplitude of vibrations, and it indicates a hardening of the lattice.

The observed changes in $\langle v^2 \rangle$ and in $\langle x^2 \rangle$ can be also

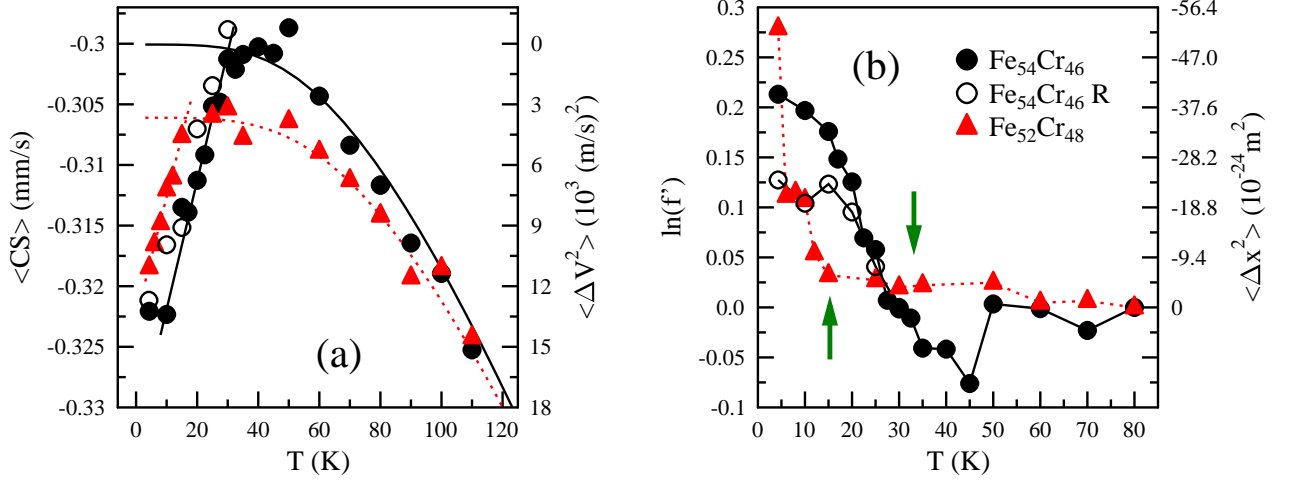


FIG. 2: (color online) (a) The average center shift, $\langle CS \rangle$, versus temperature, T , for the investigated samples: Circles stand for the $Fe_{54}Cr_{46}$ sample (full for the first run and open for the second run), while the triangles are for the $Fe_{52}Cr_{48}$. The solid and the dashed curved lines represent the behavior expected from the Debye model. Their intersection with the oblique straight lines marks the temperature at which the anomaly in $\langle CS \rangle$ starts to occur. The right-hand axis is scaled with the corresponding change of the mean-square velocity calculated from equ. (2), (b) $\ln f'$, f' being a measure for the relative recoil-free fraction, versus temperature, T , for the investigated samples. The Curie temperatures, as obtained for the two samples, are indicated by arrows.

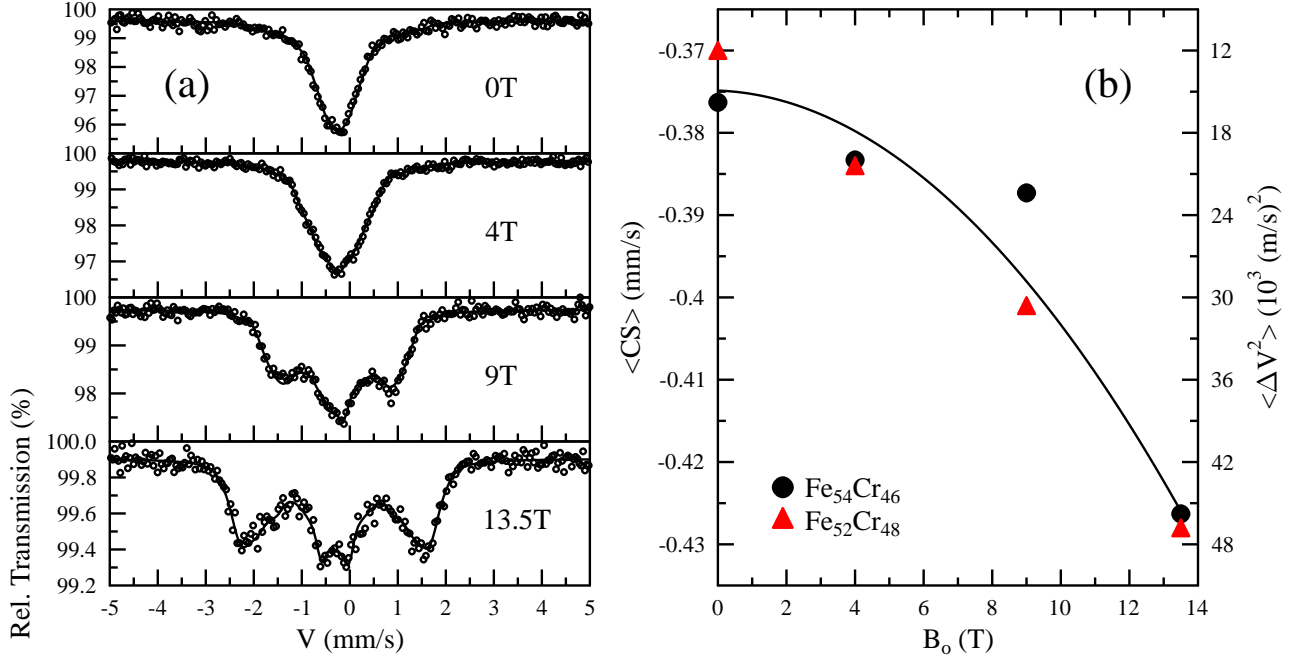


FIG. 3: (color online) (a) ^{57}Fe Mössbauer spectra recorded for the $\sigma - Fe_{54}Cr_{46}$ samples in an external magnetic field, B_0 , and (b) The average center shift, $\langle CS \rangle$, versus B_0 for the investigated samples. The solid line is a parabolic fit to the data. The right-hand axis is scaled in the corresponding change of the mean-square velocity calculated from equ. (2).

expressed in terms of underlying changes in the kinetic, ΔE_k , and in the potential, ΔE_p , energies of the vibrating atoms. A change in the kinetic energy with respect to its value at T_c for the $Fe_{54}Cr_{46}$ sample is presented in Fig. 4a. It is evident that below the Curie point, T_c , the kinetic energy increases reaching its maximum of ca.

4 meV at 4.2 K. Such a "non-thermodynamic" behavior could be related to a spin-phonon coupling which sets in on entering the magnetic state and it becomes stronger as T decreases.

The change of the potential energy in the harmonic approximation, $\Delta E_p = 0.5D\Delta\langle x^2 \rangle$, can be evaluated using

for D (a spring constant) the value of 155 N/m as found elsewhere⁸. The results obtained for the $Fe_{54}Cr_{46}$ sample are shown in Fig. 4b. It can be seen that ΔE_p show an opposite trend than ΔE_k does, as it starts to decrease at T close to T_c . At T equal to about 15 K, ΔE_p reaches the value of about 2 meV which hardly depends on T for its lower values.

Knowing changes in both forms of the mechanical energy, one can calculate a change of the total mechanical energy of the atomic vibrations, $\Delta E = \Delta E_k + \Delta E_p$, for the temperature range of interest. The behavior of ΔE , as presented in Fig. 4c, resembles that of ΔE_p i.e. it is constant below ca. 15 K, and increases steeply in the range of $\sim 15 \text{ K} < T < \sim 33 \text{ K}$. This kind of behavior follows from the fact that the dominant contribution to the observed anomaly as expressed in terms of energy is due to the potential energy. In other words, the effect of magnetism on the atomic vibrations in the studied samples manifest itself mainly via the decrease of the mean-square amplitude of vibrations, and, to a much less extent, through the accompanying increase of the mean-square velocity of these vibrations. The lack of balance in the behavior of the kinetic and the potential energy means that the vibrations are not harmonic i.e. they cannot be described properly in terms of the Debye model. However, both behaviors, could be interpreted as indicative of a hardening of the lattice vibrations caused by a magnetic state. Such behavior is, to our best knowledge, unique as previously observed anomalies were different. In particular,¹⁰ using the same technique (MS) for $DyFe_2$ a similar to ours anomaly in CS but an opposite one in f was observed. However, in that case, the material was strongly magnetostrictive, hence the observed anomalies must not necessarily be caused by the spin-phonon coupling. In our case, no traces of the magnetostriction were observed (lattice constants did not show any anomaly, and below 100 K they were hardly dependent on T), hence the observed anomalies and departure from the Debye-like dynamics seem to be directly related to the spin-phonon coupling.

In summary, we have revealed that both spectral quantities viz. the centre shift, CS , and the recoil-free fraction, f , exhibit a strong anomaly on entering the magnetic state in the studied samples. They both indicate a hardening of the lattice, which was to our best knowledge

not observed so far. Anomalous changes in CS and in f were expressed in the underlying changes in the kinetic and in the potential energy of atomic vibrations, respectively, revealing a very unusual (non-thermodynamic) behavior of the former viz. an increase with lowering temperature. This and a lack of balance between the two forms of energy ($E_p > E_k$) can be understood, if new degrees of freedom were opened below T_c . The opening might be related to the spin-phonon coupling that becomes operative when the sample becomes magnetically ordered, causing the observed lack of energy conservation and the non-Debye like vibrations.

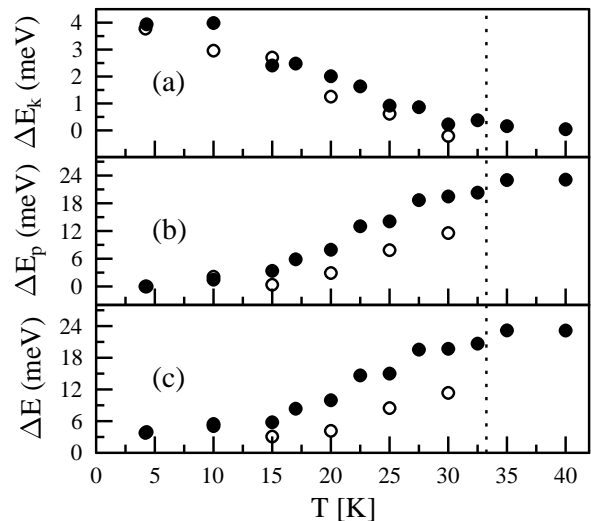


FIG. 4: Changes in the (a) kinetic, ΔE_k , (b) potential, ΔE_p and (c) total mechanical energy, ΔE versus temperature, T , as found for the $Fe_{54}Cr_{46}$ sample in the temperature range where the anomaly was observed. Full circles are for the first run and open for the second one. The dashed vertical line indicate the Curie point.

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